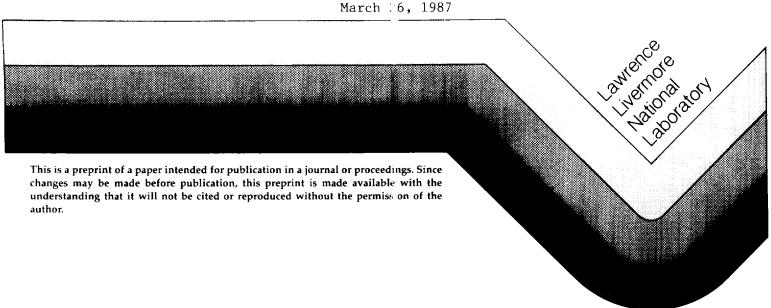Respirator Cartridge Study Using
Organic Vapor Mixtures

P. M. Swearengen
S. C. Weaver

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Lawrence
Livermore
National
Laboratory

Respirator cartridge study using organic-vapor mixtures*

P.M. SWEARENGEN and S.C. WEAVER

Lawrence Livermore National Laboratory, Hazards Control Department

P.O. Box 808, Livermore, CA 94550

INTRODUCTORY SUMMARY

We measured the performance of respirator cartridges during challenge by organic-vapor mixtures. All cartridges were tested in pairs under carefully controlled conditions of mass flow, temperature, and relative humidity. We used five chemical compounds during the testing: methyl ethyl ketone, isopropyl alcohol, hexane, n-butyl acetate, and ethyl benzene. Cartridges were challenged by a single component at first 1000 and then 2000 ppm by volume concentration, under a standard flow of 40 liters per minute. Each challenge was repeated three times for precision, and every challenge was performed separately at 50% and then at 8 % relative humidity. We chose the high concentration of each single-component challenge to equal the arithmetic total concentration of the various mixtures that were subsequently tested. We selected five different pairs of compounds to use as organic-vapor mixtures to challenge the cartridges. Chemical concentrations were monitored upstream of the cartridges by infrared analysis and downstream by gas chromatography (using a gas-sampling valve). Our results showed that the observed breakthrough times for most of the mixtures were similar to those times measured for one of the single components at the high concentration.

INTRODUCTION

Air-purifying respirators are widely used in modern industry to prevent personnel exposure to organic vapors. A significant amount of data is available in the industrial hygiene literature concerning the efficiency of respirator cartridges against challenge by different organic vapors.[1-4] The industrial hygienist can study this literature to estimate the effective use times of chemical cartridge respirators. However, the existing information has almost always dealt with challenge by a single component, though in many workplace environments the atmosphere contains a mixture of vapors. A common example of this occurs during spray painting, where both the paint solution and the thinning liquids are a mixture of organic solvents. A hygienist has almost no information available to estimate the service life of respirators used in the presence of organic-vapor mixtures. For this reason, we undertook a study to observe the response of respirator cartridges to both single-component and binary-mixture challenges.

Construction projects for research programs at the Lawrence Livermore National Laboratory (LLNL) have used large quantities of spray paints. We had several of the most frequently used paints analyzed by gas chromatography/mass spectrometry (GC/MS). In the four samples submitted for analysis, bulk-sample assay showed isopropyl alcohol (IPA), methyl ethyl ketone (MEK), butyl acetate (BA), and ethyl benzene (EB) to occur in large (percentage) amounts. We also used a fifth solvent, n-hexane (HEX), in single-component challenges to compare the respirator-cartridge response of another common solvent molecule with properties different from those of the first four.

All cartridges used in our study were from two lots produced by the same manufacturer. We tested pairs of the cartridges in a flow system under

carefully controlled conditions of mass flow, temperature, and relative

humidity (RH). The flow rate used in all experiments was 40 liters per minute

(this value corresponds to breathing during heavy work conditions, and should

represent a worst-case situation for respirator lifetime during actual use).

Cartridges were challenged by a single component first at 1000 ppm and

then at 2000 ppm. We repeated each challenge three times for precision, and

we performed every challenge separately at 50% and 85% RH. The mixtures

chosen for testing were: MEK and IPA, MEK and HEX, EB and BA, MEK and EB, and

IPA and EB. We selected these particular pairs to give combinations of

chemicals with different physical properties. We also repeated the mixture

studies three times and at the two selected humidities. The high concentration

of the single-component challenge was chosen to equal the arithmetic total

concentration of the different mixtures.

EXPERIMENTAL DETAILS AND METHODOLOGY

We conducted our experiments within a flow system that allowed precise

control and measurement of all operating parameters (Figure 1). The airstream

was generated using a Miller-Nelson Research device (Model HCS-301) that

provides control of flow, temperature, and relative humidity.[5] Solvent

concentrations of all chemicals (Mallinckrodt, AR grade or equivalent) were

carefully added to the airstream from a syringe (Hamilton Co., 1000 series,

Gastight), driven by a Sage Instruments syringe pump (Model 355). The solvent

concentration upstream from the respirator cartridges was monitored by an

infrared analyzer (Foxboro-Wilkes Co., Miran 1A). We employed multiple

syringe pumps during injection of the mixtures. Also, for the mixtures, we

performed the calibration of the infrared analyzer for one compound in the presence of the second compound. In this manner, optical-signal contributions from the second compound were taken into account over the concentration ranges used during the study.

The respirator cartridges used throughout this work were MSA Chemical Cartridges (PN 459315), Lot Number 3085 and 5184. The adsorbent material in the cartridge is a petroleum-base activated carbon, 12 x 20 mesh, manufactured by WITCO Chemical Company. MSA describes the carbon as having excellent affinity for organic vapors, and (due to its relative hardness) as producing very little dust during active use.[6] We measured the average mass of carbon per cartridge from lot no. 3085 to be 34.90 g and from lot no. 5184 to be 41.84 g.

We designed a small chamber so that the airstream would flow in parallel through a pair of cartridges simultaneously. The parallel exhaust flows were then combined downstream from the chamber, and this combined airstream was monitored for solvent concentrations. The downstream airflow was analyzed by gas chromatography using a data system that uses an integrator/minicomputer system to calculate and record results (Varian Instruments, Vista 6000, Model 401 CDS). A glass-packed column, 3m x 2mm i.d., (20% SP 2401 on 100/120 Supelcoport) was used with a flame-ionization detector in the chromatograph. Injections into the chromatograph were made from a gas-sampling valve (Valco Instruments Co. 6-port, 250 μl sample loop). The valve and the chromatography data system were controlled by a digital valve-sequence programmer (Valco Instruments DVSP-4). The bulk of the airstream was then exhausted into a fume hood.

All experimental work was conducted at both a low and a high relative humidity (RH). Work within LLNL and other work by Nelson[3] has shown that at a

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RH above 50%, the uptake of water by carbon in respirator cartridges increases

significantly. This uptake of water also decreases the breakthrough time for

organic vapors. Accordingly, the work reported here was performed under

conditions below the large uptake region, i.e. at 50% RH, as well as at a

level where water would play an important role, 85% RH. The cartridges were

tested in an "as received" condition -- taken from the carton, removed from

the plastic wrapping and placed in the system for testing. We performed no

prehumidification or drying.

RESULTS AND DISCUSSION

Table I gives a summary of the chemicals used in the cartridge testing.
Only small amounts of aliphatic components were observed to be present in the
paint. However, hexane was chosen for addition to the study because its
molecular weight and its vapor pressure are close to those of the other
compounds, and because it is a nonpolar molecule. We wanted to observe if
either of the latter two properties in a commonly used solvent molecule would
produce a measureable effect.

The compounds involved in this study can be conveniently divided into two
groups based on their physical properties. Group 1 is made up from the
molecules of low molecular weight, low boiling point, and high(er) vapor
pressure. Group 2 is made up of molecules which have high(er) molecular
weight, high(er) boiling point, and low vapor pressure. Looking at its
molecular weight and boiling point, IPA fits nicely into Group 1, along with
HEX and MEK. BA and EB are conversely placed into Group 2. When only vapor
pressure is considered, however, IPA is seen to occupy an intermediate

position. For this reason, and for the resulting breakthrough times, we will arbitrarily categorize IPA as a "swing" molecule. In this study, for reasons which may be due to its molecular properties, IPA can act as either a Group 1 or a Group 2 molecule.

Single Compound Challenges

Breakthrough curves of the five compounds at 1000 and 2000 ppm are given at 50% RH in Figure 2 and at 85% RH in Figure 3. All of the curves shown in these two figures result from use of a single compound to challenge a pair of cartridges. These results are consistent with other reported results using organic vapors on activated carbon in respirator cartridges.[1-4] With increased solvent vapor concentration, or with increased relative humidity, the vapor breakthrough time is decreased.

We observed the breakthrough time to be affected by the vapor pressure of the challenge compound. At either concentration, and at either humidity, the two Group 1 compounds with the highest vapor pressures (HEX and MEK) precede the other three compounds in breakthrough time. This separation is least pronounced at 85% RH and at 1000 ppm, and is most pronounced at 50% RH and 1000 ppm. While the proposed classification applies to the groups themselves, the order within each group is not perfect. Only a partial order of decreasing vapor pressure is seen within Group 2 during any of the four experimental cases. The difference in the breakthrough times for BA and EB is within the error of the experiment. Also, the reported difference in experimental vapor pressure for these two compounds is quite small. Observed differences in adsorption may be due to other molecular properties, for these compounds as well as for IPA.

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Mixture Tests

The first mixture studied was IPA and MEK. By our classification procedure, this would be a mixture of two Group 1 compounds. Our experiment used 1000 ppm each of the two compounds. With this mixture, the breakthrough curves of both IPA and MEK appeared closest to the curve of IPA at 2000 ppm. The 10% breakthrough time of the IPA was decreased compared to that of pure IPA, and the breakthrough time of MEK was increased relative to that of pure MEK. We observed other mixtures with the same compounds: 500 ppm IPA with 1500 ppm MEK, and 1500 ppm IPA with 500 ppm MEK. If we look at IPA alone, in every mixture we observed a breakthrough time and curve closely related to the IPA 2000 ppm case.

With MEK, the breakthrough curve started later (87 min) and was flatter, with the lowest mixture concentration of 500 ppm; at 1000 ppm, the MEK appeared sooner (74 min) and was steeper; and at 1500 ppm, it appeared soonest (70 min) and was the steepest. The latter curve most closely approximated that of the IPA 2000-ppm case in slope and overall time of appearance of the breakthrough concentrations. This fact can be best seen when the mixture curves are plotted along with the single-component curves, as in Figure 4a-c. Breakthrough time is between that of IPA 2000 ppm (77 min) and MEK 2000 ppm (62 min). One possible explanation for this difference is that MEK may compete more successfully with IPA for the available adsorption sites. In purely physical terms, MEK may weaken the non-bonded interactions between IPA molecules and the carbon surface. As a result, IPA spends less total time within the carbon bed.

A second mixture of two Group 1 compounds was studied, MEK and HEX. The MEK was accelerated in breakthrough time (55 min for 10% BT) compared to the single-component challenge (69 min for 10% BT). The hexane was slightly

retarded in its appearance (69 min in the mixture compared to 64 min as a single compound). A comparison of these two Group 1 mixtures shows that the smaller molecule appears first, with a decrease in its breakthrough time. The larger molecule is delayed in its breakthrough.

Our third mixture was with the two Group 2 molecules, EB and BA. As seen in Tables II or III, the breakthrough times of either compound in the mixture are accelerated relative to either compound alone at 2000 ppm. In each case, BA appears first. In light of our discussion with IPA and MEK, the EB may compete more successfully for the available adsorption sites; as a result, the BA spends less total time within the carbon bed. The practical industrial hygiene application is that, with the binary mixtures observed, a "high boiling" compound can be accelerated through the carbon bed. The vapors then appear sooner than would be anticipated from knowledge of the net effective concentration and single-component breakthrough times.

The third set of mixtures studied was a combination of Group 1 and Group 2 chemicals. The two pairs chosen were IPA and EB, and MEK and EB, with 1000 ppm of each compound as before. We repeated the studies at 50% RH and 85% RH. In each case, the EB did not break through at a time near that of a 2000 ppm challenge of the pure vapor; however, the EB did appear before the breakthrough time of the single-vapor challenge at 1000 ppm. With the Group 1 molecule IPA, the time of appearance was 71 min at 50% RH and 66 min at 85% RH. Both of these times are well ahead of the 2000 ppm challenge of pure IPA (92 min at 50% RH and 81 min at 85% RH, respectively). Our proposed explanation for these effects is the same as before: the number of active sites available for the IPA is reduced, or at least the attraction of IPA for the sites is decreased by the presence of the EB. With MEK, the breakthrough time is 65 minutes, while that observed for MEK alone is 62 minutes. This

-9

difference is within the error of the experiment. It does not appear that a decrease in the number of adsorption sites, or of the effective competition of MEK for those sites, occurs in this mixture as was seen with IPA and EB.

CONCLUSIONS

More work needs to be done to understand how organic-vapor mixtures affect activated-carbon respirator cartridges. In the work reported here, some insight was gained by using a classification scheme for the compounds used in cartridge testing. The molecules were grouped according to their molecular weights, boiling points, and vapor pressures. With these criteria, isopropyl alcohol, methyl ethyl ketone, and hexane (Group 1 -- the smaller molecules with lower boiling points) were categorized separately from butyl acetate and ethyl benzene (Group 2 -- the larger molecules). We observed experimentally that the Group 1 molecules methyl ethyl ketone and hexane had shorter breakthrough times than the Group 2 molecules ethyl benzene and butyl acetate. In this same single-component breakthrough study, isopropyl alcohol appeared in a time frame similar to the Group 2 compounds.

We studied a series of binary mixtures. For Group 1 combinations -- using IPA and MEK as one pair and MEK and hexane as the second -- in each case, the smaller molecule broke through first and was accelerated relative to the single-component time. With IPA and MEK, the MEK was retarded; but with MEK and HEX, both were accelerated. The larger molecule in the Group 1 combinations was delayed in breakthrough when compared with breakthrough time of the pure compound). When we studied Group 2 compounds, both compounds broke through ahead of the single-compound time. If this trend proves to be

-10-

repeatable, it may indicate need for a conservative approach to estimating effective cartridge life during mixture use. The hygienist will have to anticipate a breakthrough before that normally expected from the fastest single component alone at the same total concentration. Unless specific studies have been performed for the mixtures considered by the hygienist, it follows that some type of "end-of-service-life" indicators should be in use.

We also chose two pairs of intergroup compounds for study: IPA and EB, and MEK and EB. In these mixtures, the Group 1 molecule came through at or ahead of the breakthrough time for the pure compound; the Group 2 molecule was retarded in its breakthrough.

The generalization at this point in our study is that smaller, lighter molecules tend to appear sooner through the respirator cartridge, and that when two heavy molecules are mixed, both can appear sooner than anticipated from single-component results. These trends are consistent at both moderate and high humidity. More work needs to be done to verify the ability to predict effects based on the classification scheme presented here. Our experiments indicate that it may be possible to model organic-vapor mixture effects on respirator cartridges by a such a classification scheme.

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FIGURE CAPTIONS

FIGURE 1. The experiments with organic vapor mixtures were conducted in a flow system that allowed precise control of all operating parameters.

FIGURE 2. Breakthrough curves for all five compounds at 1000 ppm and at 2000 ppm -- 50% RH.

FIGURE 3. Breakthrough curves for all five compounds at 1000 ppm and at 2000 ppm -- 85% RH.

FIGURE 4. When the breakthrough curves for mixtures are compared with the curves for high concentrations of MEK and IPA alone, the mixture curves fall nearest to the IPA high-concentration curve.

TABLE I.
Chemical Properties of Organic Solvents

Solvent	Molecular Weight	V.P.[a] (torr)	B.P. (°C)	Sol/H_2O (%)	Polarity Index[a]
MEK	72.1	90.6	79.6	24	4.7
IPA	60.1	32.4	82.3	100	3.9
Hexane	86.2	120	68.7	0.001	0.1
n-Butyl acetate	116.2	7.8	126.1	0.43	4
Ethyl benzene	106.2	9.7	136.2	0.02	<2.3

[a] See Reference 8.

TABLE I.

Comparison of 1% Breakthrough Time for Single Components and Mixtures at 50% RH.

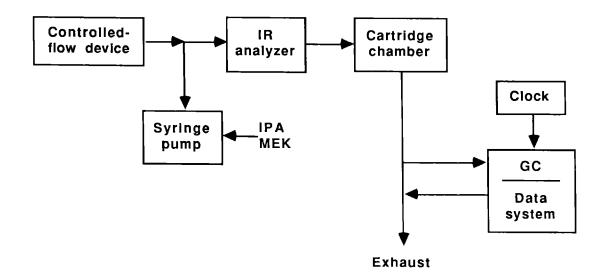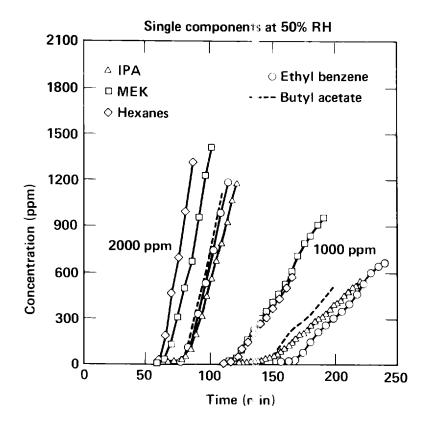| Mixture				Solvent			
Solvent	Co (ppm) 1%	BT (min) 1%	BT (min) 10%	Solvent	Conc. (ppm)	BT 1%	BT 10%
IPA	1000	57	71				
Ethyl Benzene	1000	116	141				
	1000	69	78				
	1000	74	86	IPA	2000	77	92
					1000	136	164
IPA	1500	77	90				
MEK	500	87	95				
	500	67	74				
	1500	70	82				
MEK	1000	60	68	MEK	2000	62	69
Ethyl Benzene	1000	117	137		1000	117	131
MEK	1000	50	55	Hexanes	2000	62	64
Hexanes	1000	55	69		1000	120	130
Butyl Acetate	1000	56	66	Ethyl Benzene	2000	74	84
Ethyl Benzene	1000	62	78		1000	154	174
				Butyl Acetate	2000	76	82
					1000	144	156

TABLE III.
Comparison of 1% Breakthrough Time for Single Components and Mixtures at 85% RH.

Mixture

Solvent	Co (ppm)	BT 1%	(min) 10%
IPA	1000	54	66
Ethyl Benzene	1000	106	133
	1000	62	72
	1000	67	79
IPA	1500	75	87
MEK	500	82	88
	500	63	72
	1500	65	75
MEK	1000	55	65
Ethyl Benzene	1000	122	140
MEK	1000	48	53
Hexanes	1000	53	67
Butyl Acetate	1000	56	62
Ethyl Benzene	1000	60	72

Solvent

Solvent	Co (ppm)	Bt 1%	(min) 10%
IPA	2000	73	81
	1000	125	146
MEK	2000	55	62
	1000	114	137
Hexanes	2000	60	65
	1000	112	124
Ethyl Benzene	2000	77	83
	1000	145	165
Butyl Acetate	2000	72	84
	1000	140	156

FIGURE 1

FIGURE 2

16

Single components at 85% RH

FIGURE 3

IPA/MEK 500/1500

IPA/MEK 1000/1000

IPA/MEK 1500/500

FIGURE 4

18